Rhenium Carbonyl Fluorides: Preparation, Crystal Structure, and some Properties of Hexacarbonylrhenium(I) μ-fluoro-bis[pentafluororhenate-(V)]

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The title compound $[Re^{I}(CO)_6][Re^{V}{}_2F_{11}]$ has been prepared as green (α) and yellow (β) crystalline modifications by the reaction of ReF_6 with $[Re_2(CO)_{10}]$ in anhydrous hydrogen fluoride at room temperature. Some physical properties have been examined. Crystals of the α form are orthorhombic, space group *Pnma*, with unit-cell dimensions $a = 15.30(9)$, $b = 13.64(7)$, $c = 8.16(3)$ Å, and $Z = 4$. The structure has been refined by three-dimensional least-squares methods to R 0.064 for 748 reflections measured by diffractometer. The compound contains discrete $[Re(CO)_6]^+$ and $[Re_2F_{11}]^-$ ions. The cation is closely octahedral, and the anion contains a single linear fluorine bridge linking two eclipsed ReF_6 octahedra.

THE reaction of $[Re_2(CO)_{10}]$ with ReF_6 was first studied by Hargreaves and Peacock;[1] mixtures of ReF_4O, ReF_4, and CO were produced when an excess of liquid ReF_6 was used as solvent. The present work entailed a systematic investigation of the reaction of $[Re_2(CO)_{10}]$ with ReF_6 in anhydrous hydrogen fluoride. A preliminary report of this work has appeared,[2] the chemical properties[3] and structure[4] of one of the main products obtained from this system, $[Re(CO)_5F{\cdot}ReF_5]$, have been described, and we now give details of the structure and properties of the second major product, $[Re^{I}(CO)_6][Re^{V}{}_2F_{11}]$, which appears to exist in two crystal modifications. During the course of this work, O'Donnell and Phillips[5] have reported on the same reaction, although their results differ substantially from ours.

RESULTS

A systematic investigation of the reaction of rhenium hexafluoride with rhenium carbonyl in anhydrous hydrogen fluoride was carried out, using molar proportions of $[Re_2(CO)_{10}]$: ReF_6 of 1 : 2, 1 : 3, and 1 : 4. The appropriate amounts of ReF_6 were condensed on to frozen mixtures of $[Re_2(CO)_{10}]$ and anhydrous HF and the mixtures warmed to room temperature. There was no evolution of CO in any of the reactions. The 1 : 2 reaction gave an orange-red solution from which orange crystals of $[Re(CO)_5F{\cdot}ReF_5]$ were obtained. The overall stoicheiometry of the reaction is represented by equation (1) (r.t. = room temperature).

$$[Re_2(CO)_{10}] + 2ReF_6 \xrightarrow{\text{r.t.}} 2[Re(CO)_5F{\cdot}ReF_5] \qquad (1)$$

The compound $[Re(CO)_5F{\cdot}ReF_5]$ was identified by comparison of the X-ray powder pattern and i.r. spectrum with those of ground single crystals of $[Re(CO)_5F{\cdot}ReF_5]$.[3]

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[1] G. B. Hargreaves and R. D. Peacock, *J. Chem. Soc.*, 1960, 1099.

[2] D. M. Bruce, J. H. Holloway, and D. R. Russell, *J.C.S. Chem. Comm.*, 1973, 321.

[3] D. M. Bruce, A. J. Hewitt, J. H. Holloway, R. D. Peacock, and I. L. Wilson, *J.C.S. Dalton*, 1976, 2230.

[4] D. M. Bruce, J. H. Holloway, and D. R. Russell, *J.C.S. Dalton*, 1978, 64.

[5] T. A. O'Donnell and K. A. Phillips, *Inorg. Chem.*, 1972, **11**, 2563.

When a third molar equivalent of ReF_6 was added to a solution containing 1 : 2 proportions of $[Re_2(CO)_{10}]$ and ReF_6 the solution became green. After filtering and cooling, orange prisms of $[Re(CO)_5F\cdot ReF_5]$ and green platelets separated in approximately equal amounts. No detectable carbon monoxide evolution occurred and no evidence for $[Re_2(CO)_{10}]$, ReF_6, or ReF_5 was obtained. Single-crystal *X*-ray crystallographic examination of the green material has shown that the compound is $[Re^{I}(CO)_6][Re^{V}_2F_{11}]$. A balanced equation involving equal quantities of $[Re^{I}(CO)_6][Re^{V}_2F_{11}]$ and $[Re(CO)_5F\cdot ReF_5]$ as products of the 1 : 3 reaction cannot be written although these are the main products. The presence of small quantities of other species such as ReF_5 cannot be ruled out [equation (2)].

$$[Re_2(CO)_{10}] + 3ReF_6 \xrightarrow{\text{r.t.}} [Re(CO)_5F\cdot ReF_5] + [Re^{I}(CO)_6][Re^{V}_2F_{11}] + \text{other minor products} \quad (2)$$

The reaction of $[Re_2(CO)_{10}]$ and ReF_6 in a 1 : 4 ratio produced a yellow solution. Over several days the solution turned green and a golden-yellow crystalline solid was deposited. Elemental analysis showed that the empirical formula is $[Re_3(CO)_6F_{11}]$ but the *X*-ray powder pattern and i.r. spectrum had minor differences from those of green $[Re^{I}(CO)_6][Re^{V}_2F_{11}]$. Some unchanged ReF_6, together with trace amounts of other unidentified minor products, also remained. The yield of $[Re^{I}(CO)_6][Re^{V}_2F_{11}]$ was *ca.* 86% based on total rhenium used. It was concluded that the product was a different crystalline modification of $[Re^{I}(CO)_6][Re^{V}_2F_{11}]$ produced according to reaction (3).

$$[Re_2(CO)_{10}] + 4ReF_6 \xrightarrow{\text{r.t.}} 2[Re^{I}(CO)_6][Re^{V}_2F_{11}] + ReF_6\ (\text{trace}) + \text{other minor products (trace)} \quad (3)$$

This was confirmed by dissolving yellow $[Re^{I}(CO)_6][Re^{V}_2F_{11}]$ in anhydrous HF (green solution) and evaporating to dryness. The green crystalline product had an identical i.r. spectrum and *X*-ray powder diffraction pattern to those of green $[Re^{I}(CO)_6][Re^{V}_2F_{11}]$. The green compound was designated α-$[Re^{I}(CO)_6][Re^{V}_2F_{11}]$ and the yellow β-$[Re^{I}(CO)_6][Re^{V}_2F_{11}]$. Polymorphism is a common feature amongst compounds with mononuclear cations and binuclear anions and it is perhaps significant, in this case, that the former is produced in a heterogeneous reaction, whereas the latter is obtained by precipitation from solution.

When heated in a Pyrex capillary the compound α-$[Re^{I}(CO)_6][Re^{V}_2F_{11}]$ decomposed without melting at 259 °C. Like other rhenium(V) species, both the α and β forms are extremely moisture sensitive, turning black in moist air. Even in controlled nitrogen atmospheres (10 p.p.m. H_2O, 20 p.p.m. O_2) surface darkening occurs. Pure α- and β-$[Re^{I}(CO)_6][Re^{V}_2F_{11}]$ exhibit neither e.s.r. nor n.m.r. signals in HF solution since, although the cation is diamagnetic, the d^2 rhenium(V) anion is likely to cause extensive line broadening in both techniques.

The *X*-ray powder patterns of α- and β-$[Re^{I}(CO)_6][Re^{V}_2F_{11}]$ have been compared and shown to be similar. The data have been deposited as part of Supplementary Publication No. SUP 22333 (6 pp.) (see Experimental section). The *d* spacings of the α form were indexed from the single crystal data. The most striking differences occur in the $d = 3.00$—3.50 region.

Infrared data on α- and β-$[Re^{I}(CO)_6][Re^{V}_2F_{11}]$ show bands which may be unambiguously attributed to $[Re(CO)_6]^+$ (ref. 6) in both forms. Peaks at 688, 663, and 649 cm^{-1} (α) and 680, 665 and 642 cm^{-1} (β) are $\nu(Re-F)$ modes of the anion. Only β-$[Re^{I}(CO)_6][Re^{V}_2F_{11}]$ has given a reproducible Raman spectrum, the α phase tending to decompose in the laser beam. Peaks characteristic of $[Re(CO)_6]^+$ occur at 2 196vw [a_{1g}, ν(CO)], 2 122vs [e_g, ν(CO)], 487m (sh) [t_{2g}, δ(ReCO)], and 435s cm^{-1} [a_{1g}, ν(ReC)]. There are additional peaks at 2 178vw, 718m, 707 (sh), 462m (sh), and 314vw cm^{-1}. A solution spectrum in HF gave absorptions at 2 204s and 2 134vw cm^{-1} but no clear signals were observed at lower frequencies. No attempt to make definitive vibrational assignments for $[Re_2F_{11}]^-$ has been made in view of the lack of data for other $[M_2F_{11}]^-$ species.

DISCUSSION

The results of our investigation into the reaction of $[Re_2(CO)_{10}]$ with ReF_6 in anhydrous hydrogen fluoride are summarised by equations (1)—(3); from the range of molar proportions studied, only two major products were formed. In the 1 : 2 reaction the adduct $[Re(CO)_5F\cdot ReF_5]$ is formed smoothly in high yield. With an increasing proportion of ReF_6, $[Re^{I}(CO)_6][Re^{V}_2F_{11}]$ is additionally formed such that in the 1 : 4 reaction it represents 86% of the total rhenium used. Presumably $[Re(CO)_5F\cdot ReF_5]$ is an intermediate in the formation of $[Re^{I}(CO)_6][Re^{V}_2F_{11}]$, but since no accompanying species containing less than five co-ordinated CO molecules was found the additional CO required to form $[Re(CO)_6]^+$ must come from the complete breakdown of a $Re(CO)_5$ unit. The formation of $[Re(CO)_6]^+$ under these reaction conditions contrasts with the usual methods of preparing $[M(CO)_6]^+$ (M = Mn, Tc, or Re) salts from the appropriate pentacarbonyl halide, which require high pressures of CO and a good halide acceptor.[7] In the reaction of CO with $[Re(CO)_5F\cdot ReF_5]$, $[ReF_6]^-$ is expected to be an excellent leaving group, enhancing the formation of $[Re(CO)_6]^+$ under much lower pressures of CO. This view is supported by a recent report [8] that $[Re(CO)_5F\cdot AsF_5]$ dissolves readily in liquid SO_2, a weak donor, to give $[Re(CO)_5(SO_2)][AsF_6]$ whose SO_2 group may in turn be easily displaced by ligands such as acetone and water.

The crystal structure of α-$[Re^{I}(CO)_6][Re^{V}_2F_{11}]$ consists of zig-zag rows of discrete $[Re_2F_{11}]^-$ anions sandwiched between $[Re(CO)_6]^+$ cations (Figures 1 and 2). Closest contacts between fluorine atoms of the anion and the cation atoms are: to Re, 4.13, to O, 2.85, and to C, 3.19 Å, which confirm the ionic formulation. Bond lengths and angles within the individual ions are given in Table 1.

The high standard deviations of the cation bond lengths preclude detailed comparisons with other rhenium carbonyl derivatives. Nevertheless, the mean Re–C distance is shorter than the W–C distance [2.058(3) Å] found in $[W(CO)_6]$,[9] thereby lending support to a

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[6] E. W. Abel, R. A. N. McLean, S. P. Tyfield, P. S. Braterman, A. P. Walker, and P. J. Hendra, *J. Mol. Spectroscopy*, 1969, **30**, 29.

[7] E. W. Abel and S. P. Tyfield, *Adv. Organometallic Chem.*, 1970, **8**, 117.

[8] T. A. O'Donnell, K. A. Phillips, and A. B. Waugh, *Inorg. Chem.*, 1973, **12**, 1436.

[9] S. P. Arnesen and H. M. Seip, *Acta Chem. Scand.*, 1966, **20**, 2711.

suggestion by Abel *et al.*,[6] on the basis of vibrational data, that considerable strengthening of the M–C σ bond occurs along the series $[V(CO)_6]^-$, $[Cr(CO)_6]$, $[W(CO)_6]$, $[Re(CO)_6]^+$ which balances the weakening of the M–C π-bond component. The anion consists of two ReF_6 octahedra sharing one vertex, which is on a crystallographic centre of symmetry. The bridging Re–F distance is significantly larger than the mean of the terminal Re–F distances. Rhenium–fluorine distances for a number of compounds are given in Table 2.

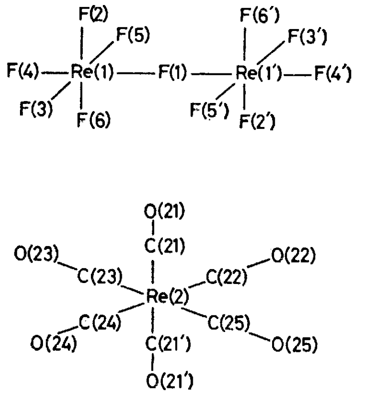

FIGURE 1 The $[Re_2F_{11}]^-$ and $[Re(CO)_6]^+$ ions showing atomic labelling

TABLE 1

Interatomic distances (Å) and angles (°) for α-$[Re^I(CO)_6]$-$[Re^V{}_2F_{11}]$ with standard deviations in parentheses

(*a*) Distances			
Re(1)–F(1)	2.009(2)	Re(2)–C(21)	1.98(3)
Re(1)–F(2)	1.85(3)	Re(2)–C(22)	2.03(6)
Re(1)–F(3)	1.89(3)	Re(2)–C(23)	2.02(6)
Re(1)–F(4)	1.79(3)	Re(2)–C(24)	1.89(7)
Re(1)–F(5)	1.84(3)	Re(2)–C(25)	2.07(7)
Re(1)–F(6)	1.84(3)	Mean Re–C	2.01(4)
Mean Re–F(2—6)	1.84(2)		
		C(21)–O(21)	1.14(4)
		C(22)–O(22)	1.12(7)
		C(23)–O(23)	1.16(8)
		C(24)–O(24)	1.19(8)
		C(25)–O(25)	1.12(9)
		Mean C–O	1.13(3)
(*b*) Angles			
F(1)–Re(1)–F(2)	87.0(0.8)	C(21)–Re(2)–C(22)	92.5(1.0)
F(1)–Re(1)–F(3)	86.9(0.8)	C(21)–Re(2)–C(23)	91.7(1.0)
F(1)–Re(1)–F(4)	179.7(1.1)	C(21)–Re(2)–C(24)	87.6(1.0)
F(1)–Re(1)–F(5)	86.6(0.9)	C(21)–Re(2)–C(25)	88.6(1.0)
F(1)–Re(1)–F(6)	86.8(0.8)	C(22)–Re(2)–C(23)	85.1(2.2)
F(2)–Re(1)–F(3)	92.4(1.2)	C(22)–Re(2)–C(24)	176.8(2.8)
F(2)–Re(1)–F(4)	93.3(1.3)	C(22)–Re(2)–C(25)	88.5(2.4)
F(2)–Re(1)–F(5)	86.8(1.2)	C(23)–Re(2)–C(24)	91.7(2.7)
F(2)–Re(1)–F(6)	173.7(1.1)	C(23)–Re(2)–C(25)	173.6(2.3)
F(3)–Re(1)–F(4)	93.1(1.3)	C(24)–Re(2)–C(25)	94.7(2.9)
F(3)–Re(1)–F(5)	173.4(1.2)	Re(2)–C(21)–O(21)	176(3)
F(3)–Re(1)–F(6)	88.4(1.1)	Re(2)–C(22)–O(22)	180(5)
F(4)–Re(1)–F(5)	93.5(1.4)	Re(2)–C(23)–O(23)	177(5)
F(4)–Re(1)–F(6)	92.9(1.3)	Re(2)–C(24)–O(24)	180(6)
F(5)–Re(1)–F(6)	91.7(1.2)	Re(2)–C(25)–O(25)	170(6)
		Re(1)–F(1)–Re(1′)	180.0

The M_2F_{11} unit has been observed in a number of crystal structures of compounds having varying degrees of ionic character (Table 3). The compound $[Re^I(CO)_6]$-$[Re^V{}_2F_{11}]$ is an example of the limiting case in which there is an isolated $[M_2F_{11}]^-$ anion in an ionic lattice. Following Davies *et al.*,[10] the structure of the $[Sb_3F_{16}]^-$ ion in $[Br_2][Sb_3F_{16}]$ [11] may be taken as the opposite extreme, *i.e.* it contains an essentially covalent Sb_2F_{11} unit. The $[Re_2F_{11}]^-$ anion consists of a linear, eclipsed, F-bridged pair of ReF_6 octahedra whereas $[Sb_3F_{16}]^-$ contains bent, staggered, F-bridged SbF_6 octahedra. However, both $[I_2][Sb_2F_{11}]$ [10] and $[SbCl_4][Sb_2F_{11}]$ [12] must be regarded as ionic judging from the length of 'anion–cation' contacts, yet both contain substantially bent Sb–F–Sb bridges. The size of the bridging angle does not therefore appear to depend only on the degree of ionic character. There is a strong correlation between the M–F–M bridging angle and the dihedral angle (ψ)

TABLE 2

Rhenium–fluorine bond lengths

		Re–F		
Compound	O.s.	terminal	bridging	Ref.
ReF_7 (vapour) [a]	7	1.835		*b*
ReF_6 (vapour) [a]	6	1.832(4)		*c*
$K_2[ReF_8]$	6	1.90(4)		*d*
$[Re(CO)_5F{\cdot}ReF_5]$	5	1.83(3) 1.91(4) [e]	1.97(2)	3
$[Re^I(CO)_6][Re^V{}_2F_{11}]$	5	1.84(2)	2.01(1)	*f*
$ReFO_3$ (vapour) [g]	7	1.859(8)		*h*
ReF_4O	6	1.86(4)	1.99(4) 2.30(4) [i]	*j*
$[NH_4]_8[Re_2F_6O_3]_4{\cdot}12H_2O$	5	2.020(9)		*k*
$K_2[ReF_6]$	4	1.953(4)		*l*
$[Re(CO)_5F{\cdot}ReF_5]$	1		2.17(4)	3

O.s. = Rhenium oxidation state for the Re–F bond in question.

[a] Gas-phase electron-diffraction study. [b] J. E. Jacob and L. S. Bartell, *J. Chem. Phys.*, 1970, **53**, 2235. [c] J. E. Jacob and L. S. Bartell, *J. Chem. Phys.*, 1970, **53**, 2231. [d] P. A. Koz'min, *J. Struct. Chem.*, 1964, **5**, 60. [e] Bond *trans* to bridging fluorine. [f] This work. [g] Gas-phase microwave study. [h] A. Engelbrecht, A. Javan, and J. F. Lotspeich, *J. Chem. Phys.* 1959, **31**, 633. [i] Bond *trans* to Re=O bond. [j] A. J. Edwards and G. R. Jones, *J. Chem. Soc. (A)*, 1968, 2511. [k] A. Pintchovski, S. Soled, R. G. Lawler, and A. Wold, *Inorg. Chem.*, 1975, **14**, 1390. [l] G. Clark and D. R. Russell, *Acta Cryst.*, 1978, **B34**, 894.

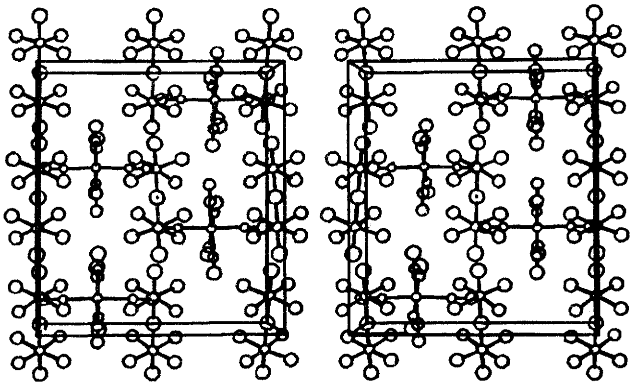

FIGURE 2 A stereoscopic view of the unit-cell contents approximately along the *c* axis

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[10] C. G. Davies, R. J. Gillespie, P. R. Ireland, and J. M. Sowa, *Canad. J. Chem.*, 1974, **52**, 2048.

[11] A. J. Edwards and G. R. Jones, *J. Chem. Soc. (A)*, 1971, 2318.

[12] H. B. Miller, H. W. Baird, C. L. Bramlett, and W. K. Templeton, *J.C.S. Chem. Comm.*, 1972, 262.

between the octahedral equatorial planes of each MF_6 unit which share the bridging fluorine atom, *i.e.* the ' twist ' angle of the two bridged octahedra.[13] Angle ψ varies from 0° with M–F–M 180°, to near the maximum of 45° when angle M–F–M is smallest at *ca.* 145°, presumably because this reduces steric repulsion between the *cis*-fluorine atoms from each octahedron which approach as M–F–M bends.

The cation $[Re(CO)_6]^+$ is well known in being amongst the most stable of simple metal carbonyl species, forming salts with a wide variety of anions, including $[PF_6]^-$ and $[AsF_6]^-$. The compound $[Re^I(CO)_6][Re^V{}_2F_{11}]$ is, however, the first occurrence of an organometallic cation with a transition-metal(v) fluoro-anion. These latter species had previously been associated only with highly fluorinated systems considered incompatible with oxidation-sensitive organometallic species. The stable coexistence of Re^I and Re^V in the same molecule in $[Re(CO)_5F{\cdot}ReF_5]$, and the same lattice in $[Re^I(CO)_6]$-$[Re^V{}_2F_{11}]$, as well as the now growing number of other organometallic compounds exhibiting widely separated oxidation states, imply a greater stability to oxidation of organometallic systems than had been appreciated hitherto.

TABLE 3

Comparison of geometry in $[M_2F_{11}]^-$ anions

Compound	Closest atom to $[M_2F_{11}]^-$ and distance (Å)	Average M–F bond (Å) terminal	Average M–F bond (Å) bridging	M–F–M (°)	ψ/°	Ref.
$[Re^I(CO)_6][Re^V{}_2F_{11}]$	O 2.85	1.84(4)	2.01	180	0	*a*
$[I_2][Sb_2F_{11}]$	I 2,89	1.85(2)	2.00	166	21	10
$[SbCl_4][Sb_2F_{11}]$	Sb 3.0	1.87(7)	2.01(7)	155		12
$[ClO_2][Sb_2F_{11}]$	Cl(2) 2.55	1.82(3)	2.01(3)	146	40	*b*
$[IF_4][Sb_2F_{11}]$	I(2) 2.51	1.86(2)	2.02(3)	156	18	*c*
$[TeF_3][Sb_2F_{11}]$	Te(2) 2.54	1.86(4)	2.02(3)	161	11	*d*
$[BrF_4][Sb_2F_{11}]$	Br 2.24	1.81	2.04(12)	173	6	*e*
$[XeF_3][Sb_2F_{11}]$	Xe 2.50	1.83	2.03(1)	155	18	*f*
$[SeF_3][Nb_2F_{11}]$	Se(3) 2.40	1.83(3)	2.05(2)	166	13	*g*
$[XeF][Sb_2F_{11}]$	Xe 2.34	1.82(7)	2.02(3)	149	33	13
$[Br_2][SbF_5{\cdot}Sb_2F_{11}]$	Sb 2.10	1.83	2.04(3)	148	42	11

[a] This work. [b] A. J. Edwards and R. J. C. Sills, *J.C.S. Chem. Comm.*, 1974, 1726. [c] A. J. Edwards and P. Taylor, *J.C.S. Dalton*, 1975, 2174. [d] A. J. Edwards and G. R. Jones, *J.C.S. Dalton*, 1973, 2150. [e] M. D. Lind and K. O. Christe, *Inorg. Chem.*, 1972, **11**, 608. [f] D. E. McKee, A. Zalkin, and N. Bartlett, *Inorg. Chem.*, 1973, **12**, 1713. [g] A. J. Edwards and G. R. Jones, *J. Chem. Soc.* (*A*), 1970, 1491.

EXPERIMENTAL

Starting Materials.—Rhenium carbonyl was obtained from Strem Chemicals Inc. (Danvers, Massachusetts, U.S.A.). Rhenium hexafluoride was prepared from the elements by the method of Malm and Selig.[14] Purity was monitored by i.r. and Raman spectroscopy. Anhydrous HF was provided by Imperial Chemical Industries (99.5% purity) and was further purified by distillation, fluorination, and redistillation.

Reactions.—The reactions were carried out using vacuum techniques in Kel-F [poly(chlorotrifluoroethylene)] apparatus. Weighed amounts of $[Re_2(CO)_{10}]$ (*ca.* 0.75 mmol) were loaded into pre-seasoned vessels under nitrogen, and HF (3 cm^3) was condensed on to the solid at -196 °C. The required amounts of ReF_6 were sublimed into the reactors which were then brought slowly to room temperature.

The reaction of $[Re_2(CO)_{10}]$ with ReF_6 in a 1 : 2 mol ratio was complete within a few minutes, giving an orange-red solution from which orange crystals precipitated. On completion of the reaction HF was removed under static vacuum. The 1 : 3 reaction required periodic warming over *ca.* 18 h. Trace amounts of solid were always present and these were filtered from the green solution. Orange and green crystals began to precipitate on cooling the filtrate to 0 °C. Crystals suitable for *X*-ray examination were obtained by decanting the solution and pumping the cystals dry *in vacuo*. Another crop of predominantly green crystals was obtained by evaporating this solution to dryness. The 1 : 4 reaction took several days for the complete precipitation of golden-yellow crystals from the green solution. The solvent was removed by decantation and the crystals pumped to dryness.

Crystals of the green compound from the 1 : 3 reaction were transferred into short lengths of capillary for crystallographic examination as described previously.[4]

Crystal Data.—$C_6F_{11}O_6Re_3$, $M = 935.6$, Orthorhombic, $a = 15.30(9)$, $b = 13.64(7)$, $c = 8.16(3)$ Å, $U = 1\,703$ Å^3, $Z = 4$, $D_c = 3.65$ g cm^{-3}, $F(000) = 1\,632$, $\lambda(\text{Mo-}K_\alpha) = 0.7107$ Å, $\mu(\text{Mo-}K_\alpha) = 226$ cm^{-1}. Space group *Pnma* or $Pna2_1$ from systematic absences; *Pnma* gave an acceptable structure solution. D_m was not measured but the cell volume is consistent with $Z = 4$ if the structure is assumed to be a close-packed lattice of carbon, oxygen, and fluorine atoms having atomic volumes of 21, 19, and 17 Å^3 respectively (calculated on the basis of covalent radii). This method correctly reproduces cell volumes for the related compounds $[\{Ru(CO)_3F_2\}_4]$,[15] $[Re_2(CO)_{10}]$,[16] and$[Re(CO)_5F{\cdot}ReF_5]$.[4]

Accurate unit-cell dimensions were obtained from precession photographs recorded by Mo-K_α radiation. Intensities of reflections with $(\sin\theta)/\lambda < 0.7$ Å^{-1} were collected from an irregularly shaped crystal mounted about the *b* axis (layers $h0l$—$h12l$) at 20 °C using a Stoë-Guttinger-Weissenberg diffractometer with monochromatic Mo-K_α radiation and an ω-scan technique. The 763 reflections

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[13] J. Burgess, C. J. W. Fraser, V. M. McRae, R. D. Peacock, and D. R. Russell, *J. Inorg. Nuclear Chem., Suppl.* 1976, 183.

[14] J. G. Malm and H. Selig, *J. Inorg. Nuclear Chem.*, 1961, **20**, 189.

[15] C. J. Marshall, R. D. Peacock, D. R. Russell, and I. L. Wilson, *Chem. Comm.*, 1970, 1643.

[16] L. F. Dahl, E. Ishishi, and R. E. Rundle, *J. Chem. Phys.*, 1957, **26**, 1750.

having $I \geqslant 3\sigma(I)$ were corrected for Lorentz and polarisation effects.

Scattering factors for neutral atoms, including full correction for anomalous scattering by Re, were taken from ref. 17, and the structure was solved by conventional Patterson and difference-Fourier techniques. Block-diagonal least-squares refinement of positional and isotropic thermal parameters for all the atoms and individual layer scale factors reduced R to 0.117. Further cycles of refinement using anisotropic thermal parameters for rhenium reduced R to 0.102. Having thus confirmed the chemical composition, an absorption correction, determined by the method of de Meulenaer and Tompa,[18] was applied. Further cycles of refinement converged with $R = 0.077$. In the final cycles 15 reflections with large discrepancies between $|F_o|$ and $|F_c|$ were excluded. The function minimised was $\Sigma w(|F_o| - |F_c|)^2$, with $w = (10 + |F_o|)^{-1}$. A final difference Fourier revealed no significant features and an analysis of the weighting scheme over $|F_o|$ and $(\sin \theta)/\lambda$ was satisfactory.

Observed and calculated structure factors and thermal parameters have been deposited as Supplementary Publication No. SUP 22333 (6 pp.).* Final positional parameters, with their estimated standard deviations, are listed in Table 4. Interatomic distances and angles are given in Table 1.

X-*Ray Powder-diffraction Measurements*.—Specimens were mounted in evacuated Pyrex capillaries and their diffraction patterns recorded photographically on a Philips 11.64-cm diameter camera with Cu-K_α filtered radiation.

TABLE 4

Final positional parameters for α-$[Re^I(CO)_6][Re^V{}_2F_{11}]$ with estimated standard deviations in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Re(1)	0.112 20(9)	−0.001 05(11)	0.127 82(24)
Re(2)	0.377 47(14)	0.25	0.108 31(34)
F(1)	0.0	0.0	0.0
F(2)	0.153(2)	−0.092(2)	−0.022(3)
F(3)	0.148(2)	0.105(2)	−0.005(4)
F(4)	0.212(2)	−0.002(3)	0.242(4)
F(5)	0.066(2)	−0.105(2)	0.242(4)
F(6)	0.060(2)	0.088(2)	0.266(3)
C(21)	0.380(2)	0.105(2)	0.097(4)
C(22)	0.267(3)	0.25	0.244(7)
C(23)	0.440(3)	0.25	0.326(7)
C(24)	0.484(4)	0.25	−0.007(10)
C(25)	0.301(4)	0.25	−0.100(9)
O(21)	0.380(2)	0.021(2)	0.099(4)
O(22)	0.206(3)	0.25	0.320(6)
O(23)	0.479(3)	0.25	0.448(6)
O(24)	0.552(3)	0.25	−0.080(6)
O(25)	0.270(4)	0.25	−0.224(7)

Infrared and Raman spectra were recorded as described previously.[3] Analysis was by a commercial analyst {Found: C, 7.70; F, 21.2. Calc. for β-$[Re^I(CO)_6][Re^V{}_2F_{11}]$: C, 7.70; F, 22.3%}.

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

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